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Peculiarities in the high-pressure phase behaviour of binary mixtures of nitrogen with methane, helium and water

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Abstract. The experimental phase behaviour of binary mixtures of nitrogen with three very different components is discussed. The phase diagrams have also been determined theoretically but with modest success. It will be shown that our knowledge of the unlike potential parameters is insufficient.

1. Experimental results

The investigations reported in this paper have been carried out in a diamond anvil cell. The equipment and experimental procedures used to obtain the coexistence surfaces have been described elsewhere [1, 2] and will not be discussed. It is sufficient to note that the experimental data on the phase equilibria have been collected by three independent methods: visual observation, Raman spectroscopy and quasi-isochoric temperature scans.

1.1. Nitrogen–methane

The first system to be discussed is nitrogen–methane. Since the intermolecular potential of the two components is very similar it is considered to be an almost ideal system. Therefore one would expect a rather small liquid–gas coexistence region and no liquid–liquid or gas–gas phase separation. The ratio of the intermolecular diameters is about 0.96. On the basis of this ratio it is to be expected that the fluid–solid phase equilibrium is of the spindle type [3].

The system has been investigated previously at low pressures and temperatures. An overview of the experimental results on the vapour–liquid equilibria and thermodynamic properties of the fluid phases has been presented by Kidnay *et al* [4]. For our purpose the detailed p – T – x analysis up to 0.2 MPa performed by Omar *et al* [5] is of particular interest. In figure 1 the fluid–solid T – x diagram at 0.2 MPa is given. The diagram is more complicated than is anticipated. Instead of the expected spindle type diagram the system shows a eutectic point with a eutectic concentration of about 24 mol% methane. At high nitrogen concentrations the solid–fluid region could hardly be measured since it is extremely narrow and nearly temperature independent. Near the eutectic point the temperature difference between the liquidus and the solidus is less than 0.5 K. This unusual behaviour is expressed by Omar *et al* by calling it a ‘degenerate’ eutectic equilibrium.

The fluid–solid phase behaviour at high pressures is rather complicated due to the various solid phases in the pure components. The discussion will be restricted to the fluid–solid equilibrium at high nitrogen concentrations because this is the most interesting part. In

Figure 1. The T - x diagram of nitrogen-methane at 0.2 MPa [5].

figure 2 part of the proposed phase diagram at 2 GPa is presented [6]. The temperature range of the fluid-solid equilibrium is much larger than that at low pressures. Moreover, the experimental results suggest the existence of a fluid-fluid equilibrium in a temperature range of 2 K, in contrast with theoretical predictions. The three-phase equilibrium denoted by the dashed line at about 250 K has been determined unambiguously by using p - T scans. Moreover, we observed visually that above this temperature the two-phase equilibrium consists of a fluid phase and another phase with a completely spherical shape. Since this happened repeatedly and with mixtures of 21 as well as 24 mol% methane we interpret this phase as a gaseous phase.

1.2. Nitrogen-helium

The nitrogen-helium system has been studied extensively, also at high pressures [7-9]. The intermolecular potentials of the two components are very different with respect to both the volume and the energy parameters. The system is considered to be far from ideal. Therefore, it is reasonable to expect phase separation in the fluid phase. The ratio of the intermolecular diameters is about 0.65. According to the hard-sphere model the mutual solubility in the solid phases vanishes for values of this ratio below 0.76. On the basis of this model it is anticipated that there is no solubility in the solid phases.

In figure 3 the T - x diagram is presented for a pressure of 6.5 GPa [8]. The system exhibits fluid-fluid equilibrium with a critical mole fraction of about 80 mol% helium. It turns out that the critical composition hardly changes between 2 and 10 GPa. This equilibrium persists to pressures far above 10 GPa [9]. The system is very interesting since at

Figure 2. Part of the proposed T - x diagram of nitrogen-methane at 2 GPa.

Figure 3. The T - x diagram of nitrogen-helium at 6.5 GPa [8].

low temperatures there is an unexpectedly high solubility of helium in solid nitrogen, which amounts to almost 10% [10], while at room temperature and high pressures a van der Waals compound is formed [11].

Helium-nitrogen mixtures have also been studied using vibrational Raman spectroscopy. We will discuss here only the measurements in the homogeneous fluid phase. The vibrational frequency of a particular molecule, e.g. nitrogen, is mainly determined by the intramolecular forces but it will be slightly modified by the intermolecular forces. The addition of a second component, in this case helium, changes the intermolecular forces and results in a shift of the vibrational frequency to higher values. The Raman shift at e.g. 4.5 GPa and room temperature varies from about 2340 cm^{-1} for pure nitrogen to about 2350 cm^{-1} in a dilute solution of 2 mol% nitrogen in helium. More interesting is the behaviour of the linewidth as a function of concentration. In figure 4 the linewidth of nitrogen in helium is plotted as a function of concentration at 4.5 GPa and room temperature [12]. The linewidth in the mixture increases by a factor of two compared to that in pure nitrogen. The curve shows a maximum at about 80 mol% helium. This is very remarkable since such a distinct maximum has not been reported previously for mixtures. We will come back to this point later.

1.3. Nitrogen-water

Finally we will consider the behaviour of mixtures of nitrogen with a polar component. In this case we are particularly interested in the shape of the critical line. Since the critical temperature of water is relatively high (about 650 K) the measurements were performed under difficult experimental conditions and therefore the accuracy is less than in the other systems.

Up to 0.25 GPa and 660 K the system has been investigated by Japas and Franck [13]. At the highest experimental temperature the critical mole fraction of water is 0.62. We have determined the fluid-fluid coexistence surface by visually observing the phase

Figure 4. The linewidth of the nitrogen vibron in nitrogen-helium as a function of composition at 4.5 GPa and room temperature [12].

Figure 5. The p - T projection of the line of constant composition in nitrogen-water, the low-pressure critical points of [13] and the critical line of [20].

separation of various mixtures as a function of temperature and pressure [14]. For a mixture with 50 mol% water, which is close to the critical composition at high temperature, our measurements extend to 750 K. Figure 5 shows the p - T projection of the line of constant composition (50%) together with the low-pressure critical points of [13].

2. Discussion

The peculiarity of the nitrogen-methane mixture is the existence of fluid-fluid equilibria for mole fractions of nitrogen around 0.25. In order to calculate the fluid phase behaviour we have used the variational perturbation theory of Ree [15]. The parameters for the α -exp-6 potential for nitrogen and methane as well as the mixture have been determined from density and sound velocity data at pressures up to 1 GPa. It is not possible to obtain a unique set of parameters since a large number of sets results in essentially the same standard deviation between calculated and experimental results. Since the parameters will be used at high pressures we have also taken into account the tendency of the deviations at high pressures. At constant p and T the Gibbs free energy of mixing has then been calculated as a function of nitrogen mole fraction in steps of 0.01. The double-tangent method was used to obtain the coexisting phases. It turned out that e.g. at room temperature and pressures up to 5 GPa separation into two fluid phases did not occur while experimentally it was found at 2.5 GPa.

Given the fact that the parameters could vary considerably we then used various consistent sets for the pure components and adjusted the unlike parameters until phase separation was obtained. A detailed description of the calculations will be reported elsewhere. Here we will only present an important result. Room temperature fluid-fluid phase separation is obtained at a pressure of 2.5 GPa for a nitrogen-methane mixture with 25% methane if the following set of unlike parameters is used: $\alpha = 15.8$; $\epsilon/k = 150$ K; $r^* = 4.10 \times 10^{-10}$ m.

The parameters obtained in this way have been tested to calculate the densities and sound velocities of methane-nitrogen using perturbation theory and to compare the results with experimental data up to 1 GPa. The agreement with the experimental densities is reasonable (1.5%); the difference from the sound velocities is about 3.5%. The agreement is certainly not perfect but even for pure components it is difficult to obtain good agreement in density and sound velocity simultaneously when using perturbation theory. The purpose

is to show that the unexpected fluid–fluid phase separation can be explained using acceptable parameters for the unlike interaction.

The fluid–fluid equilibrium in the nitrogen–helium system has been calculated using the same procedure as for nitrogen–methane. In this case also the parameters can be varied considerably before the standard deviation of the fit changes essentially. The calculations provide results opposite to those for nitrogen–methane where it was difficult to obtain phase separation theoretically. Applying perturbation theory results even at room temperature in a phase separation at about 0.5 GPa while it occurs experimentally at about 7.5 GPa. The enormous difference might be due to a failure of perturbation theory or the van der Waals one-fluid theory. Therefore, we have also used parameters obtained by comparing computer simulations in the homogeneous region with the experimental data. The results did not change essentially. Finally, we have calculated the phase separation using the method of Panagiotopoulos [16]. In this case the homogeneous region is considerably extended but the phase separation still occurs at too low pressures (2 GPa).

In single-component systems a broadening of the linewidth of the Raman spectra in the critical region is obtained due to large fluctuations in the density. One would expect similar behaviour due to concentration fluctuations but theory does not predict a critical line broadening for mixtures [17]. However, we still believe that the maximum is due to critical behaviour. It should be noted that the maximum broadening occurs for 80% helium, which is also the critical composition at this pressure or temperature (note that the critical composition hardly changes along the critical line!). Although the system is far from the critical conditions it is well known that the influence of the critical point extends over a large pressure and temperature range [18]. A critical point is a singular point in p – T – x space and, therefore, if the effect is a critical effect the broadening should decrease in all directions, starting from the critical point. Indeed, the measurements showed a decrease in linewidth in going from the critical point [12]. According to Hills [17] broadening could possibly be obtained if the longer-range hydrodynamic fluctuations in the concentration were more important. This could be effectuated by assuming that the *difference* between the potentials of the pure components is of long range.

The slope of the critical line of nitrogen–water is very flat. About 100 K above the critical temperature of water the critical pressure is less than 0.65 GPa while another 100 K higher it is estimated from our measurements to be about 1.7 GPa. Christoforakos and Franck [19] constructed an equation of state for aqueous binary mixtures at high temperatures and high pressures. The repulsive interactions are represented by the Carnahan–Starling equation for hard spheres using temperature dependent diameters. For the attractive contribution a square well potential is used. The fluid–fluid equilibrium in nitrogen–water, in particular the critical line, has been calculated by Heilig and Franck [20]. They extended the equation of state to systems in which the components have considerable differences in polarity and size. Their calculated results are also presented in figure 5. It is amazing that the phase behaviour of the rather complicated water systems can be adequately described by a relatively simple equation of state.

In summary we can say that the seemingly relatively simple nitrogen–helium and nitrogen–methane systems cannot easily be described by the existing theories. Moreover, the deviation from theory with respect to phase separation is opposite for the two systems. On the other hand the aqueous nitrogen–water system is readily described by a simple model. It is possible to achieve a much better agreement between theory and experiment in the first two systems by manipulation of the parameters for the unlike potential. Probably our knowledge of the effective unlike potential, in particular for high densities is insufficient.

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